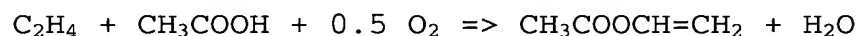


**Method for recovery of ethylene in a recirculating gas process  
for the production of vinyl acetate**

The invention relates to a process for ethylene recovery in a  
5 cycle gas process for preparing vinyl acetate, in which a sub-  
stream of the ethylenic product stream is discharged and sent  
to a process for recovering or converting ethylene.

Vinyl acetate is prepared in continuous processes with recy-  
10 cling of the purified product stream. In a heterogeneously  
catalysed gas phase process, ethylene reacts with acetic acid  
and oxygen over fixed bed catalysts which generally comprise  
palladium and alkali metal salts on a support material, and  
may additionally also be doped with gold, rhodium or cadmium.

15 The ethylene, oxygen and acetic acid reactants are reacted in  
an exothermic reaction generally at a pressure of from 8 to 12  
bar and a temperature of from 130°C to 200°C in a fixed bed  
tubular reactor to give vinyl acetate:



The ethylene conversion is about 10%, the acetic acid conver-  
sion from about 20 to 30% and the oxygen conversion up to 90%.

A problem in this reaction is that inert substances are intro-  
25 duced via the ethylene and oxygen reactants, and are difficult  
to remove, but increasingly reduce the selectivity of the re-  
action when they are recycled into the reactor and accumulate  
in the cycle gas. The inerts nitrogen and argon are introduced  
via the oxygen, and ethane and to a slight extent methane via  
30 ethylene. These inerts have to be removed continuously from  
the system, otherwise their accumulation would inhibit the re-  
action. Since ethylene constitutes the majority of the cycle  
gas mixture at from 60 to 70% by volume, the removal of inerts  
is generally accompanied by a distinct loss of ethylene of  
35 from about 1 to 4% by volume of the amount fed. In addition,  
side reactions form carbon dioxide and further by-products  
such as methyl acetate and ethyl acetate.

Owing to the incomplete conversion of the reactants, the gaseous product stream is worked up in a continuous process: in a cycle gas scrubber operated with acetic acid, the vinyl acetate target product is washed out of the cycle gas and worked up in subsequent distillation processes. The vinyl acetate-free cycle gas is sent through a cycle gas compressor to the acetic acid saturator and subsequently to the reactor. In order to reduce the CO<sub>2</sub> by-product, a portion of the vinyl acetate-free cycle gas is discharged on the pressure side of the cycle gas compressor and sent to a water scrubber. Subsequently, a small fraction is sent to incineration for inerts discharge, and the remainder is passed into a CO<sub>2</sub> absorption column and then sent back to the cycle gas in CO<sub>2</sub> free form.

The inerts discharge by means of removal of ethylene from the cycle gas prevents accumulation of ethane, methane, argon and nitrogen in the cycle gas stream. The amount of the inert stream discharged is controlled depending on the ethylene concentration in the cycle gas. When the amounts discharged are too small, the inerts become concentrated in the cycle gas and the ethylene concentration in the cycle gas falls. However, the ethylene selectivity increases with the ethylene content of the cycle gas. The higher the ethylene content in the cycle gas, i.e. the more ethylene comprising inerts from the cycle gas is removed and "fresh" ethylene is supplied, the better the ethylene selectivity is. However, from a certain proportion, a more extensive discharge of ethylene comprising inerts is uneconomic, since each additional ton of vinyl acetate monomer has to be paid for with a disproportionately high fraction of discharged ethylene comprising inerts. Since ethylene is expensive, the recovery of ethylene has the highest priority as a cost-lowering measure.

WO-A 01/00559 describes two common alternatives for ethylene recovery in vinyl acetate preparation by means of gas phase reaction of ethylene, acetic acid and oxygen. Carbon dioxide is removed from the gas stream leaving the reactor which then comprises primarily ethylene, methane, oxy-

gen, nitrogen and argon. At system pressure, the gas stream is passed into an absorption column and washed with vinyl acetate, and a mixture of methane, nitrogen, oxygen and argon is drawn off at the top of the column and sent to incineration.

5 At the bottom of the column, vinyl acetate and ethylene are withdrawn, the gas mixture is decompressed and ethylene is removed from vinyl acetate. The ethylene is subsequently compressed and passed back into the reactor.

10 Disadvantages in this context are the energy-intensive decompression-compression step, and the fact that the inerts cannot be removed fully, and thus become increasingly enriched and distinctly lower the selectivity of the reaction.

15 In a further variant, to which WO-A 01/00559 is directed, the majority of the gaseous product stream is contacted at system pressure with acetic acid in an absorption vessel. At the top of the column, methane, nitrogen, oxygen and argon are removed, and a mixture of vinyl acetate, acetic acid and ethylene is drawn off at the bottom of the column. This mixture is  
20 contacted in a gas scrubber with the remaining fraction of the gaseous product stream. The ethylene is drawn off at the top and recycled into the reactor; the vinyl acetate is obtained at the bottom of the column and sent to further workup. The decompression/compression step becomes unnecessary, but  
25 here too the inert gases accumulate increasingly in the cycle gas.

30 A similar process is the subject matter of US-A 3,714,237, in which the gaseous stream is likewise worked up by scrubbing with acetic acid, vinyl acetate is removed, and the residual gas is recycled into the reactor after the carbon dioxide has been washed out. Here too, the inert gases accumulate increasingly in the cycle gas.

35 It is therefore an object of the present invention to configure the cycle gas process in the preparation of vinyl acetate in such a way that the accumulation of the inert gases mentioned is very substantially prevented.

The invention provides a process for ethylene recovery in a cycle gas process for preparing vinyl acetate by means of  
a) heterogeneously catalysed reaction of ethylene, acetic acid  
5 and oxygen at a pressure of from 1 to 50 bar and a temperature of from 50°C to 200°C,

b) separation of the product gas stream comprising substantially ethylene, vinyl acetate, acetic acid, water, carbon dioxide and further inert gases, and

10 c) recycling of ethylene into the cycle gas process, characterized in that

d) the product gas stream is fed at system pressure to a cycle gas scrubber charged with acetic acid, and vinyl acetate is removed from the cycle gas, and

15 e) the vinyl acetate-free cycle gas is subsequently fed to a CO<sub>2</sub> absorption to remove carbon dioxide, and then

f) a portion of the ethylenic cycle gas stream is recycled into the reaction system, and the remainder of the ethylenic gas stream is discharged and reused in processes for recovering or converting ethylene.  
20

In the continuous preparation of vinyl acetate, operation is effected in tubular reactors which are charged with a fixed bed catalyst. These catalysts are generally supported catalysts doped with noble metals (or noble metal salts) and promoters, for example bentonite spheres doped with palladium and with gold (cadmium) and potassium salts. The reactor is charged with ethylene, oxygen and acetic acid, and the reaction is carried out preferably at a pressure of from 8 to 12 bar and a  
25 temperature of from 130°C to 200°C. The product gas stream leaving the reactor comprises substantially vinyl acetate, ethylene, acetic acid, water, oxygen, CO<sub>2</sub> and the inerts nitrogen, argon, methane and ethane.  
30

35 The product gas stream is subsequently separated in a cycle gas scrubber operated with acetic acid, in which vinyl acetate, acetic acid, water and further condensable fractions are removed, and the vinyl acetate monomer is obtained by means of

distillative workup. After the removal of the condensable fractions (vinyl acetate, acetic acid, water), the cycle gas typically has the following composition:

5      from 60 to 65% by volume of ethylene,  
       from 12 to 18% by volume of CO<sub>2</sub>,  
       from 5 to 8% by volume of ethane,  
       from 4 to 9% by volume of oxygen,  
       from 4 to 6% by volume of nitrogen,  
 10     from 1 to 2% by volume of argon,  
       from 0.5 to 1% by volume of methane.

This composition makes clear that, to effectively remove methane, ethane, argon and nitrogen, a relatively high proportion has to be sent to incineration, with a correspondingly high ethylene loss.

15

In the inventive procedure, the cycle gas is now conducted into a CO<sub>2</sub> absorption/desorption, customarily operated with aqueous potassium carbonate solution. After the CO<sub>2</sub> scrubbing, the cycle gas generally has the following composition:

20     from 80 to 83 % by volume of ethylene,  
       from 1 to 4 % by volume of CO<sub>2</sub>,  
       from 2 to 4 % by volume of ethane,  
       from 3 to 5 % by volume of oxygen,  
       from 3 to 4 % by volume of nitrogen,  
 25     from 0.5 to 1 % by volume of argon,  
       from 0.2 to 0.4% by volume of methane.

After the CO<sub>2</sub> scrubbing, the product stream is divided. A majority of the ethylenic cycle gas stream is recycled into the reactor via a cycle gas compressor and acetic acid saturator.

30

The remainder of the ethylenic gas stream is discharged and reused in processes for converting ethylene. Preference is given to discharging from 1 to 25% by volume, more preferably from 5 to 20% by volume, of the ethylenic gas stream. The carbon dioxide laden with traces of hydrocarbons is passed to  
 35     thermal disposal.

The recycling is effected preferably into processes for converting ethylene. Examples thereof are oxidation processes for

preparing acetaldehyde and for preparing acetic acid, the oxy-chlorination of ethylene for preparing dichloroethane and the direct chlorination of ethylene to dichloroethane. Further examples are the preparation of ethylene oxide and ethylene glycol, alkylation of benzene to ethylbenzene and optionally dehydrogenation to styrene, the carbonylation to acrylic acid, the polymerization to polyethylene, the hydroformylation to propionaldehyde, the Reppe carbonylation to propionic acid, and the Alfol process for preparing long-chain, primary alcohols. The ethylene may also be used for recycling in processes for refining hydrocarbons.

With the process according to the invention, the inerts discharge is no longer inevitably associated with the incineration of the valuable ethylene raw material. Virtually 100% utilization of the ethylene is possible; typically, 2% of the ethylene used is lost as a result of the inerts discharge. The generation of environmentally polluting carbon dioxide owing to ethylene incineration is prevented. This corresponds to a drop of 50 kg of CO<sub>2</sub> per metric ton of vinyl acetate monomer.

The examples which follow serve to further illustrate the invention:

Figure 1 shows a simplified diagram of the process:

Example 1:

A 25 m<sup>3</sup> tubular reactor 1 which was equipped with a Pd/Au supported catalyst was charged at a pressure of 8.5 bar and a temperature of 160°C via line 2 with a gas mixture having a gas hourly space velocity (GHSV) of 3500 h<sup>-1</sup>. The gas mixture (cycle gas) had the following composition:

61.7% by volume of ethylene,

10.8% by volume of CO<sub>2</sub>,

12.7% by volume of acetic acid,

3.4% by volume of ethane,

8.0% by volume of oxygen,

0.8% by volume of nitrogen,

0.8% by volume of argon,  
1.0% by volume of methane  
0.8% by volume of water.

5 The cycle gas leaving the reactor 1 was fed via line 3 to a  
vinyl acetate scrubber 4 operated with acetic acid, and subse-  
quently via line 6 to a carbon dioxide scrubber 7 operated  
with potash. A vinyl acetate/acetic acid/water mixture was  
10 withdrawn via line 5 from the vinyl acetate scrubber 4 and  
sent to further processing. After the carbon dioxide scrub-  
bing, 200 kg/h, corresponding to approx. 7% by volume, of the  
cycle gas going to the CO<sub>2</sub> removal were passed via line 8 into  
the acetic acid preparation for ethylene recovery, and the re-  
mainder was recycled via line 9 and the cycle gas compressor  
15 10 into the reactor 1. The CO<sub>2</sub> discharge for thermal disposal  
was effected via path 11.

Under these conditions, the catalyst exhibited a space-time  
yield of 650 g/l·h at an ethylene selectivity of 91.5%.

#### 20 Example 2:

The procedure was analogous to Example 1, with the difference  
that, after the CO<sub>2</sub> scrubbing, 300 kg/h, i.e. approx. 10% by  
volume, of the cycle gas going to the CO<sub>2</sub> removal, have been  
discharged. This increased the ethylene content in the cycle  
25 gas to 64% by volume; the other components were adjusted cor-  
respondingly. The reaction conditions (GHSV, cycle gas pres-  
sure, etc.) remained the same.

The increase in the amount discharged resulted in an increase  
in the space-time yield to 660 g/l·h with an improvement in  
30 the ethylene selectivity to 92.5%, which corresponds to an at  
least 0.5% increase in the vinyl acetate production.

#### Example 3:

35 The procedure was analogous to Example 1, with the difference  
that, after the CO<sub>2</sub> scrubbing, 450 kg/h, i.e. approx. 15% by  
volume, of the cycle gas going to the CO<sub>2</sub> removal have been  
passed into the acetic acid preparation for ethylene recovery.  
This resulted in an increase in the ethylene content in the

cycle gas to 66% by volume; the other components were adjusted correspondingly. The reaction conditions (GHSV, cycle gas pressure, etc.) remained the same.

5 The increase in the amount discharged resulted in an increase in the ethylene selectivity to 93.0%, which corresponds to a 1% increase in the vinyl acetate production.